PART 5

LM FOOD CHAIN

Chapter 5. Calibration

5.5.1 Introduction

Calibration is a step of model development necessary for accurate parameterization and simulation. Before a food web bioaccumulation model is used to predict future contamination levels in fish or to address other related environmental issues, it needs to be calibrated to refine certain species- and chemical-specific parameters to site-specific conditions. The extensive collection in 1994 and 1995 of data on congener-specific polychlorinated biphenyl (PCB) concentrations in fish food webs and in water and sediment of Lake Michigan provided an excellent data set for model calibration.

5.5.2 Description of Process

The food web model was calibrated with site-specific conditions for lake trout in three biota zones and for a lake-wide coho salmon population. The calibrations were conducted for 40 PCB congeners or co-eluters individually. For each lake trout food web, the 1994-1995 measured data of PCBs in water and sediment, and temperature profiles in the associated biota zone, were used as model inputs. They were assumed to be representative of life-long average exposure condition. This assumption is appropriate because there are no congener-specific PCB exposure concentrations available prior to 1994, the decline in PCB concentrations in the lake has slowed down in recent years, and post-exposure input has a limited impact on the model output for a recent date. The dynamic food web model was run continuously until a steady-state was reached for model outputs. The obtained model outputs were considered to be the model estimates of PCB concentrations in the fish food web in response to the exposure inputs. The model predicted concentrations of individual PCB congeners were then compared to the observed PCB concentrations in the biota zone for species in each trophic level of the food web. During the calibration process, selected parameters (i.e., food assimilation efficiency (β), chemical assimilation efficiency (α), chemical relative gill transfer coefficient (E_c/E_o), and specific dynamic action (SDA)) were adjusted to improve agreement between model results and measured PCB data for the food web. The adjustments of the calibrated parameters were constrained within the limits defined by the accepted range of the parameters. Starting at the bottom of the food web, parameter adjustment and refinement was conducted for each species to identify the optimal combination of the parameters which yielded the best agreement between model results and field data for all PCB congeners. This process was repeated for all trophic levels in the food web.

The resulting calibrated parameters were then examined for all species across trophic levels to ensure that the parameter values among trophic levels and among chemical hydrophobicities were internally consistent and that their trends over trophic levels and hydrophobicities were in agreement with those reported in the literature. If necessary, the calibration process was repeated by altering the optimal combination of parameters until the calibrated parameters agreed with generally accepted trends.

Similar calibrations were done for PCBs in the Lake Michigan coho salmon. Given the available information, it was not possible to construct a dynamic food web structure to reflect variable diets of the migratory coho salmon in the lake. The coho salmon model was calibrated with three fixed food web structures. They were constructed by combining an average dietary composition of coho salmon with one of the forage food web structures from the three lake trout biota zones.

The model calibration described in this chapter was based on observed PCB data at a single point in time (1994-1995). This model calibration focused on individual PCB congeners (rather than total PCBs alone) in all age classes of the top predator as well as their entire supporting forage base. The use of constant exposure history, as represented by the 1994-1995 field data for PCBs in water and sediment, in this model calibration was an appropriate approximation. Our model test indicated that, within a certain range, the variation in past exposure concentrations had only minor impacts on the model output for current contaminant levels in fish. The uncertainty in the model calibration associated with the constant exposure history was well below the uncertainty from other sources, such as variability in food web structures and PCB field data.

5.5.3 Calibration Results

The parameter values that generated the best agreement between modeled and measured PCB data were considered to be the best estimates of the calibrated parameter set for modeling PCBs in each food web. The calibrated results for the *Diporeia* submodel are listed in Table 5.5.1. Other calibrated parameter values for each lake trout food web are given in Tables 5.5.2 and 5.5.3. A range of values was given in the tables for the chemical assimilation efficiencies of fish and *Mysis*. They were treated as functions of hydrophobicity of individual PCB congeners. The correlation of the chemical assimilation efficiency α to the hydrophobicity (or K_{ow}) of a PCB congener was adopted from the work of Gobas *et al*. (1988):

$$\text{For } \log K_{ow} < 6: \quad \alpha = 0.5$$

$$\text{For } \log K_{ow} > 6: \quad \frac{1}{\alpha} = 5.3\,(\pm 1.5)\cdot 10^{-8}\cdot K_{ow} + 2.3\,(\pm 0.3) \qquad (5.5.1)$$

This relationship was selected because it offered the best overall calibration results for congeners with different hydrophobicity.

There are considerable variations in the reported values of chemical assimilation efficiency at a given $\log K_{ow}$ value (Buckman *et al*., 2004; Gobas *et al*., 1988; Muir and Yarechewski, 1988; Niimi and Oliver, 1983; Stapleton *et al*., 2004; Thomann *et al*., 1992). There are also indications that chemical assimilation efficiency may be a function of species (Gobas *et al*., 1988; Muir and Yarechewski, 1988). However, adequate information was not available to support derivation of a species-specific assimilation efficiency. For simplicity, they were assumed to be independent of the species. The chemical assimilation efficiency used in this study are at the low end of the literature reported values (Buckman *et al*., 2004; Gobas *et al*., 1988; Stapleton *et al*., 2004). We believe that the lower values may better represent chemical assimilation in the real environment. This is because chemical assimilation efficiencies were mostly estimated based on laboratory studies using manufactured fish foods spiked with contaminants. The contaminants coated on the foods are likely to be more susceptible to digestion and thus more available for absorption by fish than contaminants accumulated naturally by prey species in the lake. Therefore, the actual chemical assimilation efficiencies for species in the real environment may be lower than what were reported.

Table 5.5.4 gives the calibrated parameters values for coho salmon which yielded the best overall agreement between modeled and observed data for all three supporting forage food webs.

The calibrated value for a particular model parameter is apparently related to other parameter values. For example, the estimated value of the food assimilation efficiency, β, is largely influenced by our selection of the chemical assimilation efficiency, α. If higher than those expressed by Equation 5.5.1, the calibrated values of the food assimilation efficiency listed in

Table 5.5.1. Calibrated Parameter Values for *Diporeia* Submodel

Parameter	Calibrated Value
Water ventilation rate across the respiratory surface, G_w (L/day)	6.0E-03
Food ingestion rate, G_d (g-dry/day)	1.8E-04
Fraction of food absorbed, β	5%
Organic carbon assimilation efficiency, α	46%
Chemical assimilation efficiency from diet, E_d	0.72
Chemical assimilation efficiency from water, E_W	0.60

Table 5.5.2. Calibrated Model Parameters for PCBs in the Sturgeon Bay and Saugatuck Lake Trout Food Webs

	Chemical Assimilation Efficiency (α)	Food Assimilation Efficiency (β)	Chemical Relative Gill Transfer Coefficient (E_c/E_o)	Energy Fraction for Specific Dynamic Action (SDA)
Zooplankton	0.15	0.60	0.7	
Mysis	0.50-0.22	0.80	1.0	0.18
Deepwater Sculpin	0.50-0.22	0.60	0.7	0.15
Slimy Sculpin	0.50-0.22	0.65	0.5	0.15
Bloater (Age 1-3)	0.50-0.22	0.25	0.4	0.18
Bloater (Age 4-7)	0.50-0.22	0.40	0.4	0.18
Alewife (Age 1-2)	0.50-0.22	0.90	0.7	0.00
Alewife (Age 3-7)	0.50-0.22	0.40	0.5	0.18
Rainbow Smelt	0.50-0.22	0.60	0.4	0.00
Lake Trout (Age 1-4)	0.50-0.22	0.40	0.6	0.15
Lake Trout (Age 5-12)	0.50-0.22	0.20	0.6	0.18

Table 5.5.3. Calibrated Model Parameters for PCBs in the Sheboygan Reef Lake Trout Food Web

	Chemical Assimilation Efficiency (α)	Food Assimilation Efficiency (β)	Chemical Relative Gill Transfer Coefficient (E_c/E_o)	Energy Fraction for Specific Dynamic Action (SDA)
Zooplankton	0.15	0.35	1.0	
Mysis	0.50-0.22	0.90	1.0	0.15
Deepwater Sculpin	0.50-0.22	0.45	0.8	0.18
Slimy Sculpin	0.50-0.22	0.50	0.7	0.15
Bloater (Age 1-3)	0.50-0.22	0.20	0.3	0.18
Bloater (Age 4-7)	0.50-0.22	0.35	0.4	0.18
Alewife (Age 1-2)	0.50-0.22	0.90	0.7	0.00
Alewife (Age 3-7)	0.50-0.22	0.40	0.5	0.15
Rainbow Smelt	0.50-0.22	0.55	0.3	0.00
Lake Trout (Age 1-4)	0.50-0.22	0.45	0.7	0.18
Lake Trout (Age 5-12)	0.50-0.22	0.25	0.8	0.18

Table 5.5.4. Calibrated Model Parameters for PCBs in Lake Michigan Coho Salmon

	Chemical Assimilation Efficiency (α)	Food Assimilation Efficiency (β)	Chemical Relative Gill Transfer Coefficient (E_c/E_o)	Energy Fraction for Specific Dynamic Action (SDA)
Coho Salmon (Age 1)	0.3	0.8	1	0.18
Coho Salmon (Age 2)	0.6	0.6	0.5	0.18

Tables 5.5.2 and 5.5.3 would have to be adjusted upward. Therefore, the value of a parameter in the tables can not be viewed or used independent of those of other parameters.

Model parameterization is also influenced by the quality of the available field data. For model calibrations conducted with limited field data that include only a few chemicals and an incomplete food web (species or age classes), model parameterization can be biased toward certain species or chemical properties with which it was calibrated. With the help of the extensive data collection, which covers a large number of chemicals with a wide range of hydrophobicities and a more complete account of species and age classes of a food web, the calibration results in Tables 5.5.1-5.5.4 is believed to be less biased and more applicable to a wide range of chemical contaminants and food webs in the lake.

5.5.4 Field Data for PCBs in Fish and Their Comparisons to Calibrated Model Outputs

Except coho salmon, Lake Michigan fish samples were collected in three biota zones in 1994 and 1995. Phytoplankton and zooplankton were collected for the same time periods in the biota zones. Plankton samples were collected by pumping and separating into phytoplankton and zooplankton (< 102 µm and > 102 µm, respectively). Coho salmon samples were collected from various locations in 1994 and 1995. Information regarding the sampling stations, collection procedures, sample preparation, and methods for PCB analysis are available in detail (U.S. Environmental Protection Agency, 1997a,b). For lake trout, samples were further classified into age classes. The method for age classification is available from Lake Michigan Mass Balance Study Methods Compendium (U.S. Environmental Protection Agency, 1997a) and Madenjian *et al.* (1998a,b, 1999).

For lake trout and its forage species, PCB data exhibited no temporal variation over the two-year period of 1994-1995. Median values for congener-based PCB concentrations in each age class or size class of a species were calculated for each biota zone. For coho salmon, PCB data showed considerable temporal variation due to their rapid growth. Whole lake median values for the concentrations of individual PCB congeners in coho salmon for different seasons (size class) were estimated. The resultant values of the observed PCB concentrations in Lake Michigan fish, *Diporeia, Mysis,* and zooplankton in 1994-1995 are presented in Appendix 5.5.1. This comprehensive PCB data set made the Lake Michigan food web model calibration probably the most complete and systematic in terms of the completeness of the food web structure and the range of hydrophobicities of chemical contaminants, among reported model studies for chemical bioaccumulation in a food web.

The agreement between simulated model outputs and observed field data is an important measure of the quality of the simulated food web model. Appendix 5.5.2 illustrates overall comparison between calibrated model results and observed concentrations of individual PCB congeners for all species in the three lake trout food webs. To facilitate the comparison, the measured PCB data for zooplankton, *Mysis*, and *Diporeia* were converted to wet-weight basis. A dry fraction of 15% was assumed for zooplankton and *Mysis*, and 20% for *Diporeia* in the lake. Each data point in the plots denotes the model result for an individual PCB congener and the corresponding field measurement. For forage fish and *Mysis*, observed PCB data were reported for composite samples of several age classes. The maximum and minimum age classes included in the composite samples were identified. An average value of the model results for the encompassed age classes was used to represent the model estimate for the PCB concentration in the composite sample and was compared with the observed composite data. For example, bloater (> 160 mm) at Sturgeon Bay represents a composite sample of bloater with age classes ranging from four to seven years old. Therefore, in Appendix 5.5.1, each measured PCB congener concentration for bloater (> 160 mm) was plotted against an average value of modeled concentration for age four through age seven bloaters. The solid line in each of the figures in Appendix 5.5.2 indicates the position of the "perfect match" between the model simulation and the observed data.

Among lake trout food webs in the three biota zones, calibration results for Sturgeon Bay and Saugatuck agree with the observed data reasonably well for most species from zooplankton to the top predator, as demonstrated by the strong positive correlations between modeled and measured PCB congener concentrations. The results indicate that the quality of model simulations increases with the trophic level of modeled species. This observation is consistent with the fact that the field measurements for PCBs in highly contaminated fish species are usually less variable and better defined than the field PCB data for less contaminated forage fish and invertebrates in lower trophic levels. The apparent model biases for overestimating or underestimating PCBs in zooplankton, *Mysis*, and *Diporeia* may be attributed to possible errors in the presumed values for water content in these invertebrates used for converting dry-weight based PCB data to wet-weight based values.

Overall the model yielded a satisfactory result for congener-specific PCBs in the top predator – lake trout. For forage species which is not specifically targeted in most previous model studies, the model results could be improved by adjusting the chemical assimilation efficiency individually for each species. However, we decided to limit the parameter adjustment to minimize the risk of turning the calibration into a mere curve-fitting exercise. Considering the large variability in the measured congener-specific PCB data for water, sediment, and organisms which were used either as exposure input or for the comparison to the model output of the calibration and considering the constraints imposed on congener-specific model parameters, the agreement between the calibrated and measured congener-specific PCB data shown in Appendix 5.5.2 are remarkable.

The calibrated parameter values which result in good fits for fish PCB data at Saugatuck and Sturgeon Bay did not yield good model results for Sheboygan Reef fishes in comparison with the observed data. In order to improve the agreement between model results and the observed fish PCB data for the Sheboygan Reef biota zone, a different set of calibrated parameter values was required. The parameter values calibrated specifically for Sheboygan Reef are given in Table 5.5.3. After the additional parameter refinement, satisfactory agreement was obtained between the simulated and observed PCB concentrations for the food web at Sheboygan Reef (Appendix 5.5.2).

For the lake-wide coho salmon, there were three calibrated model results associated with different forage food web inputs. With a common set of calibrated model parameters (Table 5.5.4), each of the calibrated model results agreed reasonably with the observed data for coho salmon. As an example, calibrated results associated with the Saugatuck forage food web are compared in Figure 5.5.1 with the observed PCB data for coho salmon at different life stages. The figure shows that except for the second year coho salmon in spring (April-May), the calibrated model results agree reasonably well with the observed PCB data for coho salmon over the season. The discrepancies for the second year coho salmon in spring probably result from a mis-characterization of the coho salmon growth curve (Table 5.4.9b). Due to large variability in fish weight at a given age and a gap in weight data collection, the estimated weight-age relationship may not properly reflect the fish growth curve in the early days of two year-old fish. The resulting growth rate may be smaller than what was actually the case. A small growth rate indicates a slow dilution process for chemicals in fish, which results in a build-up of chemicals in the fish and, consequently, a model overestimate of chemicals in fish (see Figure 5.7.5).

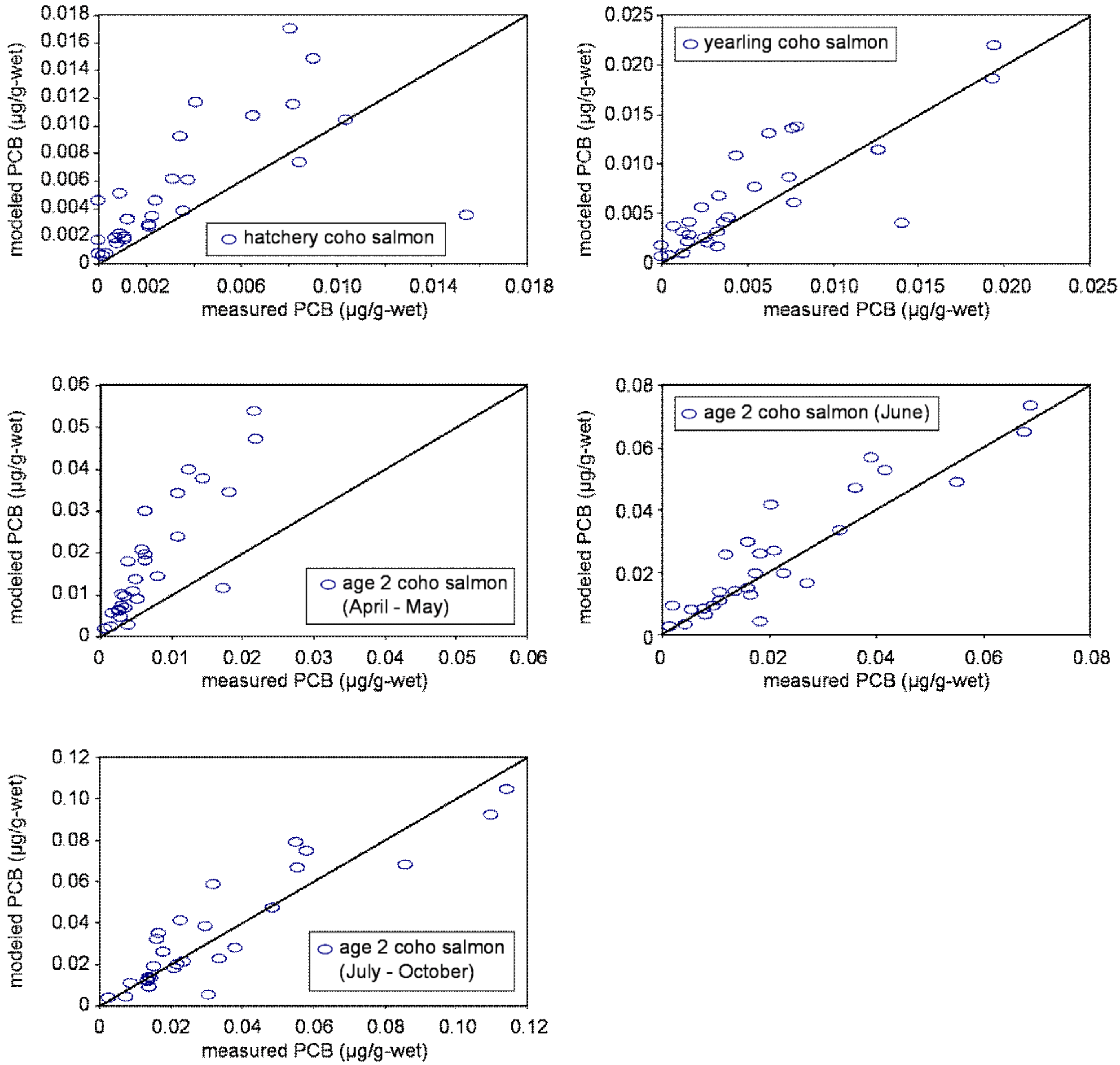

Figure 5.5.1. Agreement between modeled and observed fish PCB concentrations in coho salmon using Saugatuck food web (1994 and 1995).

Further refinement of the weight-age relationship for the fish may help reduce the discrepancies between modeled and observed spring PCB data for two year-old coho salmon.

Appendix 5.5.2 shows that the calibrated models overestimated the concentrations of most PCB congeners in young lake trout, specifically one and two year-old lake trout at Sturgeon Bay and one and three year-old lake trout at Saugatuck. It is possible to improve the agreement for these young age classes if model parameters were allowed to be adjusted independently for individual age classes. However, in this study, model parameters were defined to be species-specific or assigned to age groups (young or adult) of a species. Therefore, they were not individually refined for each age class. Rather, they were optimized systematically for all age classes or combined age classes of a species. The restriction of excessive parameter calibrations is important to reduce the risk of the calibration process being a mere curve-fitting exercise. The discrepancy between the modeled and the observed PCB data for the young lake trout does not necessarily indicate the model's limitation. In fact, this discrepancy may be attributed to the difference in the environmental condition between model simulated and the real one occupied by the young lake trout. Lake trout is a stocked species in Lake Michigan (Holey *et al.*, 1995). Before it was exposed to the lake environment and associated food webs, it was reared in hatchery facilities around the lake (Peck, 1979; Rybicki, 1990) and was exposed to a controlled environment and food. It is likely that the manufactured fish foods used in the hatchery facilities were less PCB-contaminated than the natural food items used in the food web models. Therefore, the stocked young lake trout should have lower PCB concentrations than that estimated by the food web model. An incorporation of the exposure environment in hatchery facilities into the current model framework may improve the calibrations for the young lake trout. Until then, higher predicted PCB levels in the young lake trout are expected.

A similar argument can be made for the calibration results of young coho salmon, another stocked species. Figure 5.5.1 shows that, with exception of few PCB congener data, the model results for young coho salmon were generally higher than the observed ones for most PCB congeners.

In order to evaluate the agreement between modeled and observed data in relation to the hydrophobicity of individual PCB congeners, an individual comparison was made for each PCB congener. As an example, the PCB congener data for all age classes of the lake trout at Saugatuck are illustrated in Figure 5.5.2. The results indicate that the calibrated model performed equally well for PCB congeners over a range of different hydrophobicities (log K_{ow} ranges from 5.6 to 7.71). For all PCB congeners, the modeled and observed data agreed well, taking into consideration of the uncertainty associated with the measured PCB data for individual congeners.

No comparison could be made of the current calibration to other modeling studies in terms of model performance. No similar modeling attempt has been reported to reproduce congener-specific PCB data for an entire aquatic food web. Most previous calibrations were focused on total PCBs only and were usually performed for adult predators without consideration of model results for forage species. While current calibrations yielded good agreements between the simulated and observed congener-specific PCB concentrations, it is interesting to see how well the calibrated models perform in terms of the total PCB concentrations. Modeled total PCB data in this study were estimated by summing model results for individual PCB congeners and scaling the sum based on the ratio of total PCBs to the sum of the targeted congeners from the 1994-1995 observed data. For Saugatuck lake trout, the ratio was 1.369. Figure 5.5.3 illustrates the comparison between modeled and observed total PCB data for all age classes of lake trout at Saugatuck. The result indicates that the calibrated food web model reproduces total PCB concentrations in the lake trout and its bioaccumulation trend for the age classes reasonably well.

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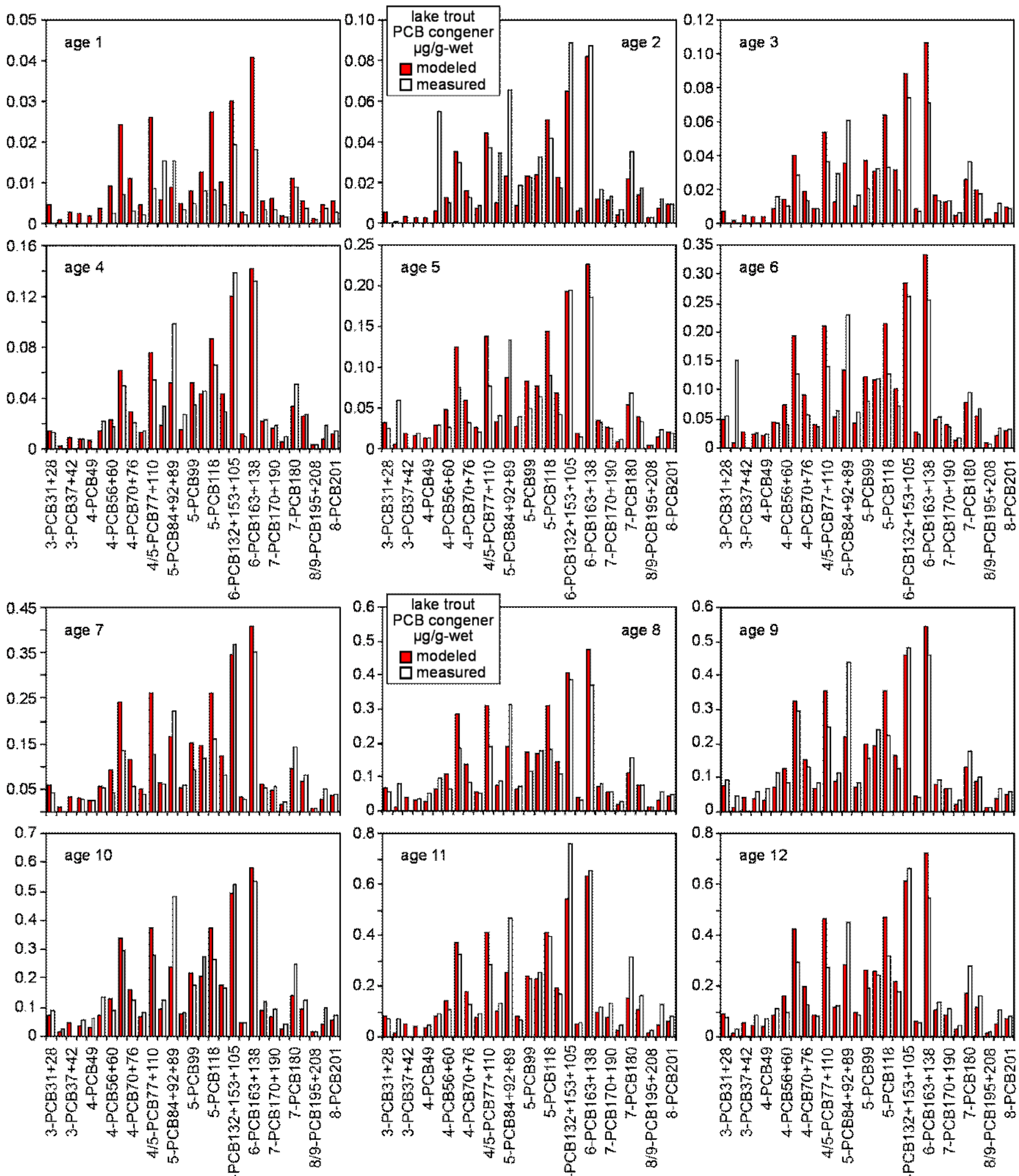

Figure 5.5.2. Individual comparison between modeled and observed data for PCB congeners in lake trout at Saugatuck (1994 and 1995).

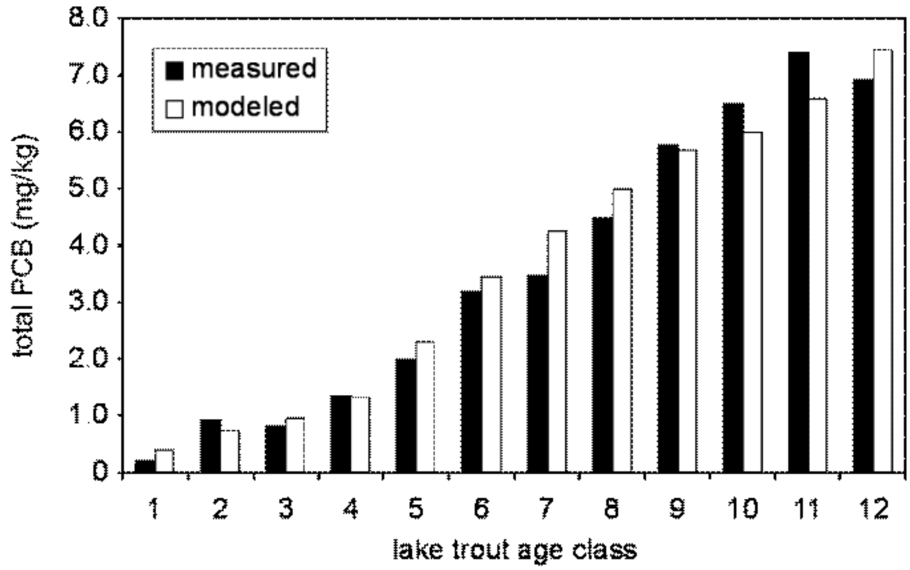

Figure 5.5.3. Comparison between modeled and observed total PCBs for lake trout at Saugatuck (1994 and 1995).

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